

Production of reducing sugars from corn stover by electrolysis

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Abstract In this study, an electrochemical system composed of a Ti/IrO₂–Pt plate as the anode and a Ti plate as the cathode was employed for the treatment of corn stover to afford reducing sugars. The optimum conditions, following the experimental design methodology of Taguchi, were electrode spacing, current density, and NaCl addition of 10 mm, 30 mA cm^{−2}, and 2000 mg L^{−1}, respectively. The recovery of reducing sugars under optimum conditions reached 0.610 mg mL^{−1} at 180 min, demonstrating the greater efficacy of this process compared to ozone pretreatment (0.297 mg mL^{−1} at 180 min). Indirect oxidation by hypochlorous acid generated in the bulk solution was a significant contributor to lignocelluloses oxidation. An increase in temperature and variation in pH during electrolysis enhanced the oxidation. After electrochemical treatment, the lignocellulosic structure was destroyed and became disordered, the crystalline index decreased from 0.4396 to 0.3493, indicating the efficacy of the described electrochemical method for converting lignocelluloses to reducing sugars. After the electrolysis, the structure of lignocelluloses became disordered, and the crystalline index decreased from 0.4396 to 0.3493, indicating that the electrolysis was an effective method for converting the lignocelluloses to the reducing sugars.

Keywords Electrochemical conversion · Corn stover · Taguchi methodology · Reducing sugars · Electrochemical oxidation

1 Introduction

In the United States, more than 80 million tons of corn stover are processed per year [1]. In contrast, the amount of corn stover processed per year in China is 220 million tons, which is significantly higher than in the United States. The mismanagement of corn stover has the potential to severely affect both air quality and human health. Corn stover consists primarily of lignocelluloses, which are comprised mainly of three different types of polymers: cellulose (37.5 %), hemicelluloses (22.4 %), and lignin (17.6 %) [2]. Corn stover is recognized as a renewable biomass resource with significant potentials for development owing to its abundant and rich cellulose content [3]; this renewable resource can be used for the generation of fuels and chemicals. The current production of bio-ethanol (first generation bio-fuels) relies on the starch and sugar sourced from food crops [4]. Accordingly, greater attention has been focused on second generation bio-fuels produced from lignocellulosic biomass owing to the limitations of first generation bio-fuels [5].

The three polymers common on biomass cellulose, hemicelluloses, and lignin are associated with each other; cellulose is tightly covered by lignin and hemicelluloses, and thus making it very difficult for cellulases to access their substrates [2].

Therefore, it is necessary to explore pretreatment processes for destroying the lignocelluloses formation, and disrupting the crystalline cellulose structure to make them more available for the enzymatic hydrolysis [6]. Various

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physical [2] and chemical pretreatments were employed. The chemical pretreatments, such as acid [7] or alkaline pretreatments [8], result in an unfavorable pH for the fermentative microorganisms unless neutralized [9]. Moreover, the above-mentioned approaches focused on destroying the lignocelluloses structure and were not concerned about the reducing sugars production, such as glucose and xylose production.

In the recent years, a few advanced oxidation processes (AOPs), such as the ozone pretreatment [10] and hydrogen-peroxide preoxidation [11], have gained significant attention because it did not contain any residual toxic substances for the downstream process [11]. Electrolysis, as another AOP, has been recognized as an attractive method for oxidizing organics [12] by generating free radicals. A green electrolysis approach involving the production of hypochlorous acid (HOCl)-containing solution has also been used for the delignification of wheat straw [13].

Moreover, the Taguchi methodology of the design of experiments (DOE) is a powerful and efficient statistical tool that allows a maximum number of main effects to be estimated in an unbiased (orthogonal) fashion with a minimum number of experimental runs to predict the optimization for the multifactor process [14]. The Taguchi methodology has been used in multiple areas such as corn stover saccharification [15] and electrocoagulation–electroflotation [16]. In electrolysis, current density, electrolyte, and electrode spacing (ES) are important parameters; the Taguchi methodology could thus be employed for the optimization of electrochemical conversion of corn stover.

In this study, in order to develop a direct conversion technology for the production of reducing sugars from corn stover, the Taguchi methodology was applied for the optimization of electrochemical conversion. The mechanism of electrochemical conversion and the behaviors of the reducing sugars during the electrolysis were also investigated.

2 Materials and methods

2.1 Materials and electrochemical apparatus

Corn stover was collected from Changping District of Beijing, China, dried at 40 °C for 48 h, and stored at 4 °C. Before the electrochemical conversion experiments, the corn stover was cut into pieces of 4–8 mm in length and 1–2 mm in width and thickness.

As shown in Fig. 1, a batch electrochemical cell was designed with a working volume of 480 mL (length 6 cm × width 5 cm × height 16 cm). Ti/IrO₂–Pt plate was employed as the anode (15 cm × 4.3 cm, TohoTech, Japan) and Ti plate as the cathode (15 cm × 4.3 cm). In

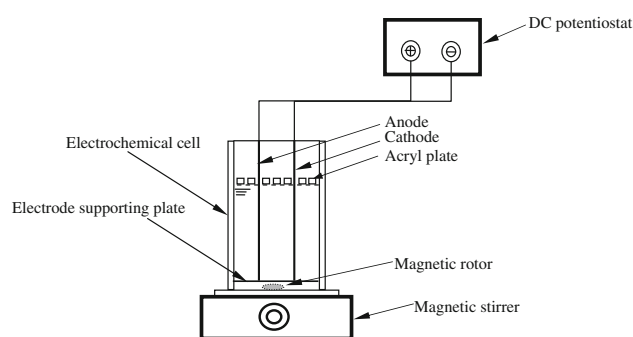


Fig. 1 Schematic diagram of electrochemical treatment

Table 1 Design of processing parameters and levels for electrochemical conversion

Parameters	Levels					
	1	2	3	4	5	6
Current density (mA cm ⁻²) (A)	5	10	20	30	40	50
NaCl addition (mg L ⁻¹) (B)	2,000	3,000	4,000	–	–	–
ES (mm) (C)	10	25	40	–	–	–

order to adjust the ES to a desired value, 14 pieces of acrylic plate (1 cm × 1.5 cm) were fixed on the walls of the electrochemical cell. A DC potentiostat (HY 1792-25, Yaguang, China) with voltage and current ranges of 0–50 V and 0–2 A, respectively, was used as a power supply. A magnetic stirrer (H01-1C, Chijiu, China) was used to homogenize the solution in the electrochemical cell.

2.2 Experimental procedure

2.2.1 Determination of optimum conditions

The DOE was performed based on the Taguchi methodology to investigate the effects of three parameters on the production of reducing sugars by electrolysis. The three parameters were current density (six levels), NaCl addition (three levels), and ES (three levels). Therefore, the L₁₈ (6¹ × 3²) mixed-level orthogonal array was selected, and the parameters and levels for the electrochemical conversion are listed in Table 1.

The corn stover pieces (1.5 g) were added into the electrochemical cell, followed by the addition of 300 mL deionized water, thus the immersed anode area (electroactive area) was 40 cm². The electrolysis was performed for 240 min for 18 trials under the specific conditions designed by the Taguchi methodology. After the electrolysis, the residual pieces were filtered, dried at room temperature, and stored in a refrigerator at 4 °C in hermetic bags with serial numbers. For each run, a 5 mL solution

was sampled from the cell at 0, 10, 30, 60, 120, 180, and 240 min for determining the concentration of reducing sugars by the 3,5-dinitrosalicylic acid (DNS) assay and measuring the pH using a pH meter (AS-211, Twin, Japan). Solution temperature was recorded at 10 min intervals using a thermometer (XY-033, Xiya Instrument Co., China).

2.2.2 Oxidation of reducing sugars

In general, organics would be oxidized during the electrolysis; therefore, it was necessary to study the behavior of the produced reducing sugars. Glucose and xylose, selected as representatives for the reducing sugars, were electrolyzed. Glucose and xylose solution were prepared by dissolving D-(+)-glucose (Sinopharm, China) and D-(+)-xylose (Sinopharm, China) (500 mg each) in 500 mL deionized water in volumetric flasks, respectively. Both glucose and xylose solutions (300 mL each) were electrolyzed for 240 min under the optimum condition as described in Sect. 2.2.1. A 1 mL sample was taken at the electrolysis time of 0, 10, 30, 60, 120, 180, and 240 min and diluted to 20 mL with deionized water in headspace bottles. The bottles were then sealed using sealing films until the samples were analyzed. The total carbon (TC) and inorganic carbon (IC) contents in each sample were determined using a total organic carbon analyzer (TOC-V CPN, Shimadzu, Japan). The total organic carbon (TOC) was calculated by subtracting the IC from the TC.

2.2.3 Comparison with ozone pretreatment

The ozone pretreatment of corn stover was conducted as a control experiment to evaluate the performance of the electrolysis method. The corn stover pieces (1.5 g) and deionized water (300 mL) were added into the electrochemical cell, and ozone gas was sparged continuously for 240 min at a flow rate of 1 L min⁻¹ using a spring purification ozone generator (SPT, China). A magnetic stirrer was used for homogenization, and a 5 mL solution was sampled from the cell at 0, 10, 30, 60, 120, 180, and 240 min for determining reducing sugar concentrations.

2.2.4 Effect of temperature and pH

To determine the effect of increasing temperature on saccharification, the electrolysis experiments were conducted at different temperatures (20, 40, and 60 °C) and the temperature was controlled using a water bath (HH-2, Zhongxing, China). The corn stover pieces (1.5 g) were added to Erlenmeyer flask under each temperature condition, mixed with deionized water, and 4000 mg L⁻¹ NaCl solution (300 mL each), respectively.

The effect of pH variation on the production of reducing sugars during the electrolysis was studied at initial pH values of 6, 7, 8, and 9 (adjusted by adding 1 M HCl and NaOH). The corn stover pieces (1.5 g) and deionized water (300 mL) were added to the electrochemical apparatus and the electrolysis experiments were performed under various pH conditions at 20 °C in the absence of an electric field. For each batch experiment, a 5 mL sample was taken from the cell at 0, 10, 30, 60, 120, 180, and 240 min for determining reducing sugar concentrations.

2.3 Reducing sugars analysis

The DNS reagent, which contains 3,5-dinitrosalicylic acid (3.15 g L⁻¹), sodium potassium tartrate (91 g L⁻¹), NaOH (20 g L⁻¹), phenol (2.5 g L⁻¹), and sodium sulfite (2.5 g L⁻¹), was stored in the dark at room temperature for 7 days prior to use. A calibration curve with R^2 of 0.999 was created using the appropriate reducing sugar concentration range. Each 4 mL sample was mixed with 4 mL DNS reagent in a 25 mL colorimetric tube. The solution was heated at 100 °C for 5 min and cooled to ambient temperature, followed by the addition of 17 mL deionized water into the tube; the tube was then turned rapidly upside down three times. Solution absorbance at 540 nm was recorded using an ultraviolet spectrometer (DR 5000, HACH, Ames, IA, USA).

2.4 Electrochemical analysis

Cyclic voltammetry experiments were performed with a computer-controlled electrochemical workstation (CHI660D, Chenhua, China) using a three-electrode cell. Ti/IrO₂-Pt, Hg/HgCl, and Ti electrodes were selected as the working, reference, and counter electrodes, respectively. The NaCl electrolyte (2000 mg L⁻¹) was mixed with the electrochemically treated materials (1.5 g corn stover pieces or 1.0 mg mL⁻¹ glucose or xylose) at 20 °C. The potential was scanned at a scan rate of 10 mV s⁻¹ starting from 0 V in the scan range of -2.0 to 2.0 V.

2.5 Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses

The SEM study was performed using a field emission scanning electron microscope (SSX-550, Shimadzu, Japan) to monitor the changes in corn stover morphology before and after electrochemical treatment.

The XRD analysis was performed to calculate the crystalline index (CrI) of the corn stover. The crystallinity of the chippings before and after electrochemical treatment was measured using an X-ray diffractometer (D8 focus, Bruker, Germany). The CrI was calculated by the following equation:

Table 2 Analysis of the L_{18} ($6^1 \times 3^2$) mixed-level orthogonal array

Trial	Current density (mA cm ⁻²)	NaCl addition (mg L ⁻¹)	ES (mm)	MCRS (mg mL ⁻¹)
1	5	2,000	10	0.456
2	5	3,000	25	0.146
3	5	4,000	40	0.154
4	10	2,000	10	0.579
5	10	3,000	25	0.318
6	10	4,000	40	0.162
7	20	2,000	25	0.267
8	20	3,000	40	0.104
9	20	4,000	10	0.483
10	30	2,000	40	0.448
11	30	3,000	10	0.545
12	30	4,000	25	0.209
13	40	2,000	25	0.238
14	40	3,000	40	0.448
15	40	4,000	10	0.402
16	50	2,000	40	0.176
17	50	3,000	10	0.425
18	50	4,000	25	0.136
Average responding				
Levels	A	B	C	
1	0.252	0.3607	0.4817	
2	0.353	0.331	0.219	
3	0.2847	0.2577	0.2487	
4	0.4007			
5	0.3627			
6	0.2457			
Range	0.155	0.103	0.2627	

$$CrI = (I_{002} - I_{am})/I_{002}, \quad (1)$$

where I_{002} is the scattered intensity at the main peak for cellulose I , and I_{am} is the scattered intensity of the amorphous portion evaluated as the minimum intensity between the main and secondary peaks.

3 Results and discussion

3.1 Electrochemical conversion performance

3.1.1 Optimization of reducing sugars recovery

The experiments were carried out under conditions according to the L_{18} ($6^1 \times 3^2$) mixed-level orthogonal array and the DOE of the Taguchi methodology. The maximum concentrations of reducing sugars (MCRS) for

each operating cycle (240 min) under the specific conditions are listed in Table 2.

According to the average response as shown in Table 2, the optimum conditions for reducing sugars production were ES, current density, and NaCl addition of 10 mm, 30 mA cm⁻², and 2000 mg L⁻¹, respectively. The relatively shorter ES favored the production of reducing sugars because of the change in hydrodynamic conditions and the decrease in internal resistance. The concentration of reducing sugars first increased and then decreased with increasing current density. This variation might be because of the oxidative production and degradation of the reducing sugars during the electrolysis experiment as explained later. As for NaCl addition, lower NaCl concentrations resulted in the greater accumulation of reducing sugars, indicating that more reducing sugars might be oxidized under a higher NaCl concentration [17].

Trial 19 was conducted under the optimum conditions, which were obtained by the analysis on Table 2. Figure 2 shows the profiles of the reducing sugar concentrations in trial 19 (ES 10 mm; NaCl addition 2,000 mg L⁻¹; current density 30 mA cm⁻²), compared to trials 4 (ES 10 mm; NaCl addition 2,000 mg L⁻¹; current density 10 mA cm⁻²), 10 (ES 40 mm; NaCl addition 2,000 mg L⁻¹; current density 30 mA cm⁻²), 11 (ES 10 mm; NaCl addition 3,000 mg L⁻¹; current density 30 mA cm⁻²), and 17 (ES 10 mm; NaCl addition 3,000 mg L⁻¹; current density 50 mA cm⁻²), in which reducing sugars production was relatively larger during the 240 min operation. As shown in Fig. 2, the reducing sugar concentrations in trials 10, 11, 17, and 19 increased at the beginning of the operation and then decreased with respect to treatment time, whereas in trial 4, it increased continuously during the experiment with a relatively slower rate. The reducing sugar concentrations increased from 0 to 0.448 and 0.425 mg mL⁻¹ in trials 10 and 17, respectively, after electrolysis for 120 min and then decreased with longer treatment time. However, in trials 11 and 19 at 180 min, MCRS were 0.545 and 0.610 mg mL⁻¹, respectively. In trial 4, the reducing sugar concentrations increased to 0.579 mg mL⁻¹ at 240 min. The MCRS in trial 19 was the highest among all the trials, confirming that the results obtained from the trials using the Taguchi methodology were reliable. Moreover, the decrease in trials 10, 11, 17, and 19 indicated that the production and degradation of reducing sugars might occur simultaneously during the electrolysis. Clearly, the ES was the primary factor affecting the production of reducing sugars based on the range of values in Table 2, followed by current density, and NaCl addition. This phenomenon was different from the behaviors of electrochemical systems for geosmin treatment [18], in which current density and NaCl addition had a greater influence on treatment outcome and ES was not observed to be a the primary factor. This result might be attributed to the differences in mass transfer environments

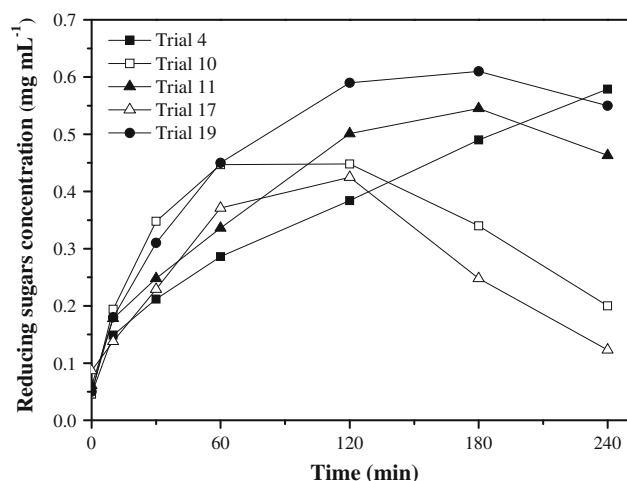


Fig. 2 Reducing sugar concentration at different electrolysis times in trial 4, 10, 11, 17, and 19

between solutions containing nitrate or geosmin and the solution mixed with corn stover fragments. In this study, the uniform diffusion of the produced oxidants on the surface of the corn stover might be difficult. This conclusion could provide guidelines for the application of electrochemical conversion methods of corn stover in the future.

As observed from Fig. 2, electrochemical performance under the conditions of trial 19 was much better than that under trial 10. Although the concentration of reducing sugars was slightly higher over the first 60 min of electrolysis in trial 10, the accumulation of larger amounts of reducing sugars was observed in trial 19 after 60 min. This result could be explained by the fact that the smaller ES functioned to enhance mass transfer and electric field intensity.

Mass transfer is well known as one of the four primary steps of the general electrochemical reaction mechanism: mass transfer to electrode; adsorption to and desorption from the electrode; direct electron transfer at the electrode; and bulk chemical reactions preceding and/or following the electron transfer. Mass transfer has often been reported to be the crucial and limiting step of the overall kinetics [19]. The decrease in the ES was beneficial to the overall reactions because it (a) shortened the distance of convection and diffusion; (b) enhanced the concentration gradient as well as lessened the mass transfer resistance; (c) strengthened the electric field intensity between the electrodes and accelerated electrolyte movement, which led to a decrease in the boundary layer thickness at the electrode surface; and (d) favored the formation of stronger turbulences and thus accelerated the dispersion of Cl_2 (g) into the solution [20]. Furthermore, the accelerated ion movement increased the conductivity and decreased the internal resistance. Consequently, the efficiency of the electrochemical conversion was improved when the ES employed was smaller.

The reducing sugars in trial 19 accumulated at a much faster rate than in trial 4. The reducing sugar concentrations in trial 11 were higher than in trial 17; the concentration decreased rapidly at 120 min in trial 17, whereas it started to decline slowly at 180 min in trial 11 (Fig. 2). This could be explained by the fact that under a higher current density, the production of more oxidants increased oxidation of both lignocelluloses and reducing sugars. Although concentrations of reducing sugars in trials 11 and 19 were similar, their concentration in trial 19 was higher than in trial 11 (Fig. 2) because of the oxidation of more reducing sugars at a higher NaCl concentration.

Higher current density indicates stronger electric field intensity; the addition of more NaCl resulted in closer isopleths, which accelerated ion movement from the solution to the electrode surface. Cl^- ions could be oxidized to Cl_2 (g) at the anode. Therefore, the generation of Cl_2 was augmented with the increase in current density and NaCl addition. However, the behavior of the reducing sugars was not proportional to Cl_2 production because the reducing sugars could be oxidized by the oxidants produced during electrolysis.

3.1.2 Electro-oxidation of reducing sugars

The electrochemical oxidation of glucose and xylose was conducted to verify the degradation of reducing sugars along with their production during electrolysis. The TOCs of both glucose and xylose solution decreased with time; the TOCs of the glucose and xylose solutions at 240 min were 0.043 and 0.034 mg mL^{-1} , respectively. In contrast, the IC of the glucose and xylose solutions at 240 min increased from 0 to 0.123 and 0.039 mg mL^{-1} , respectively. The IC consisted of HCO_3^- and CO_3^{2-} ions, which were the reaction products derived from CO_2 and H_2O . The solutions were prepared using deionized water without added CO_2 , which implied that most of the CO_2 was generated from the reducing sugars. The controlled experiments showed that the degradation of reducing sugars produced during electrolysis indeed occurred, indicating that the oxidants produced during electrolysis might also have a negative effect on the accumulation of reducing sugars. Thus, the operating conditions and electrolysis time should be optimized to maximize the production of reducing sugars and minimize energy consumption. The optimum conditions confirmed by the Taguchi methodology in this study are as follows: ES 10 mm; current density 30 mA cm^{-2} ; NaCl addition 2000 mg L^{-1} ; and electrolysis time 180 min.

3.1.3 Comparison with ozone pretreatment

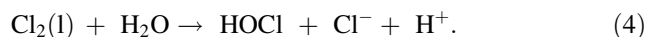
Ozone pretreatment of corn stover was also conducted for comparison to evaluate the performance of the proposed

electrochemical conversion. The concentration of reducing sugars increased during ozone pretreatment, reaching 0.297 mg mL^{-1} at 180 min, which was much lower than the MCRS (0.610 mg mL^{-1} at 180 min) in trial 19. Furthermore, the energy cost was also estimated in this study. As a result, 1 kWh electricity consumption could recovery 3,187.2 mg reducing sugars during the electrochemical treatment, whereas 544.5 mg reducing sugar in ozone pretreatment. Ozonolysis is carried out by passing ozone molecules through several water layers before absorption onto the carbohydrate surface; once adsorbed, ozone reacts slowly with C–O and C=O functional groups of lignin and hemicelluloses. Alternatively, ozone may also be dissolved in the solution before diffusing into the reaction sites [21]. Ozone dissolved in deionized water could also form a hydroxyl radical that could either increase carbohydrate oxidation or react with lignin to form aromatic alcohols [11].

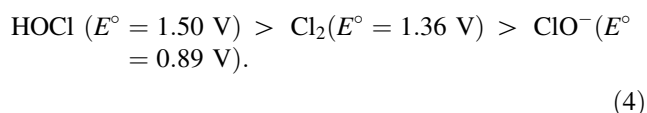
In conclusion, electrochemical treatment was shown to be an effective method for the conversion of corn stover to reducing sugars compared to ozone pretreatment.

3.2 Identification of direct and indirect oxidations

As shown in Fig. 3, the absence of the anodic peak in the cyclic voltammogram indicated that indirect oxidation played an important role in the degradation of lignocelluloses, glucose, or xylose during the proposed electrolysis. Previous reports have stated that the generation of hydroxyl radicals using a Ti/IrO₂–Pt anode was insignificant [22]. Cl[–] was mostly oxidized to Cl₂ (g) at the Ti/IrO₂–Pt anode. The conversion of chloride to HOCl is described in Eqs. (2)–(4):



The oxidizing abilities of the active chlorine species are as follows [23]:



Previous studies have confirmed the existence of different active chlorine species in solution, such as chloride, chlorine, hypochlorite, and chlorate, at various pH values. At a low pH, free chlorine was the main species, whereas at high pH chlorate ion was the dominant species. HOCl can be produced steadily only under moderately alkaline or neutral conditions [24]. Li et al. [12] reported the positive effects of HOCl generated during electrolysis on the degradation of phenol. Because of the wide-ranging production

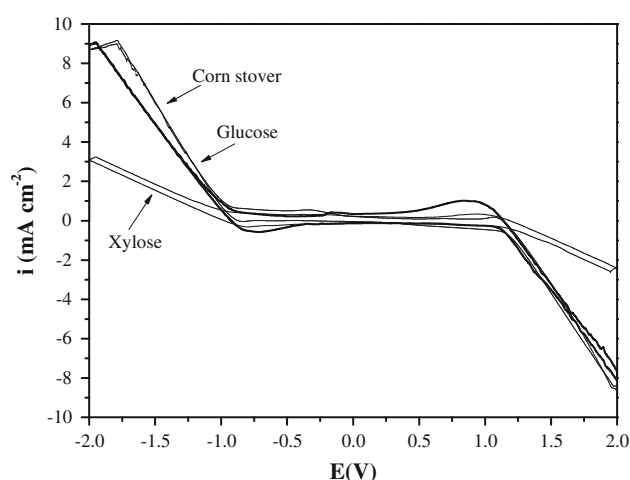


Fig. 3 Cyclic voltammogram of Ti/IrO₂–Pt plate obtained at a scan rate of 10 mV s^{-1} , NaCl addition of 2000 mg L^{-1} , with 1.5 g corn stover or 1 mg mL^{-1} glucose or xylose, respectively, 20°C (E vs. Hg/HgCl)

and consumption of oxidants, the pH values in all trials varied between 6 and 9 (Fig. 4), indicating that HOCl was the primary oxidant during electrolysis.

The effect of NaCl addition of varying concentrations on the dissolution of reducing sugars was also investigated in this study. It was found that the concentration of reducing sugars without added NaCl (Fig. 5) was almost the same as that in the presence of 4000 mg L^{-1} NaCl (data not shown) at 20, 40, and 60°C , indicating that NaCl had a minimal effect on the dissolution of reducing sugars in the absence of an electric field. However, NaCl was converted to HOCl, which played a role in lignocellulosic degradation.

The Cl–O bond of HOCl is prone to dissociation, generating Cl⁺ because of the distribution of the Mulliken charges and Cl–O bond length ($r_{\text{H–O}} < r_{\text{Cl–O}}$) in HOCl [25]. Electrophilic aromatic substitution and electrophilic addition to conjugated double bonds and other olefinic double bonds of lignocelluloses have been observed [26]. This could make the lignocelluloses convert easily into reducing sugars, such as D-(+)-glucose and D-(+)-xylose. However, the reducing sugars could be oxidized in electrolysis [27]. In the presence of HOCl, the aldehyde and hydroxyl groups of the reducing sugars would be oxidized to carboxylic acid and finally to CO₂.

3.3 Evaluation of heating and chemical effects

Heating the electrolyte during electrolysis might have a detrimental effect on current efficiency. However, the energy consumption under rising solution temperatures may not be wasted in the electrochemical treatment of corn stover. The rising temperature might have a beneficial heating effect on the accumulation of reducing sugars. It

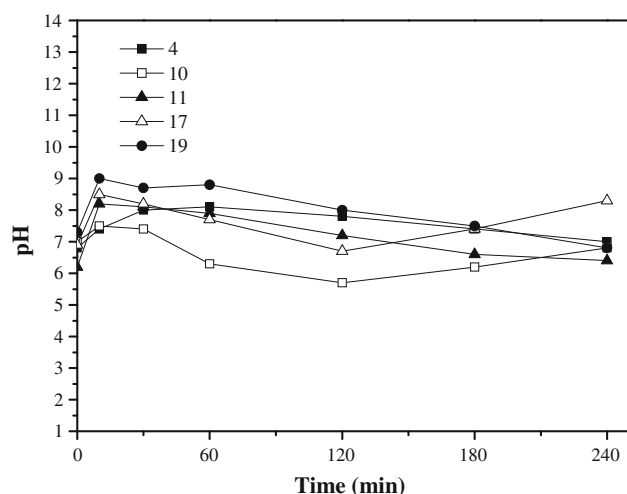


Fig. 4 Variations of pH values in trial 4, 10, 11, 17, and 19

was observed that the temperature increased in trial 19, it was 24 °C (0 min), 39 °C (60 min), 43 °C (120 min), 46 °C (180 min), and 47 °C (240 min); therefore, the heating effect on the accumulation of reducing sugars should be further investigated. The concentrations of the reducing sugars at 20, 40, and 60 °C without added NaCl are shown in Fig. 5. As evidenced from the figure, larger amounts of reducing sugars were obtained at the higher temperature. The reducing sugars gradually rose with time, and their concentrations at 20, 40, and 60 °C at 180 min were found to be 0.167, 0.195, and 0.412 mg mL⁻¹, respectively. Moreover, to further investigate the production of reducing sugars in trial 19 at different temperatures, an additional experiment was performed in a flask containing 1.5 g corn stover pieces and 300 mL NaCl solution (2000 mg L⁻¹). The temperature was adjusted manually

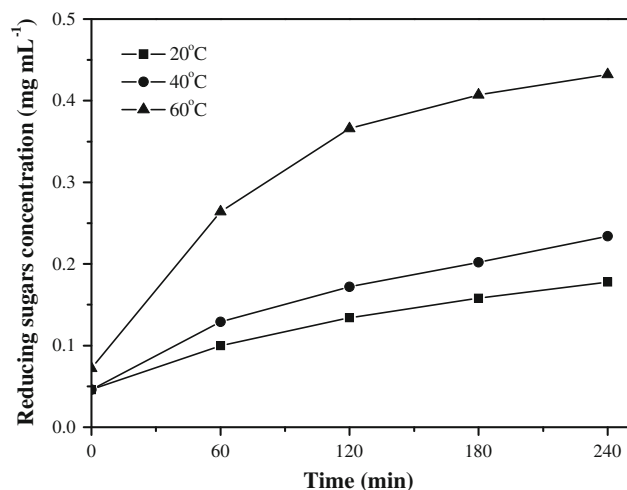


Fig. 5 Reducing sugar concentration at different temperatures and 0 mg L⁻¹ NaCl

using a water bath as in trial 19. As a result, the reducing sugar concentration reached 0.306 mg mL⁻¹ at 180 min, indicating that an increasing temperature had a synergistic effect on hydronium ion generation and reaction rate acceleration. Therefore, the electrochemical oxidation doubled the production of reducing sugars even though the degradation of the reducing sugars occurred during electrolysis.

Larger concentrations of hydronium ions were generated through water autoionization in solution with time at higher solution temperatures [28]. Hydronium ions are suggested to act as a catalyst, reacting at the most susceptible heterocyclic ether bonds of hemicelluloses, leading to the generation of oligosaccharides [29]. Moreover, the heating effect could increase the rate constant and accelerate diffusion during the electrolysis process. Therefore, the increase in temperature had a significant heating effect on enhancing the production of reducing sugars in electrochemical treatment of corn stover.

Solution pH is an important parameter in the chemical production of reducing sugars (acid or alkaline pretreatments). A possible mechanism for the acid pretreatment involves the hydrogen ion as catalyst to facilitate the hydrolysis of hemicelluloses to oligosaccharides and monosaccharides by reacting at the heterocyclic ether bonds of hemicelluloses [29, 30]. The mechanism of alkaline pretreatment is believed to be the saponification of intermolecular ester bonds crosslinking xylan hemicelluloses and other components [30].

Variations in solution pH from 6 to 9 were measured during the electrolysis experiments (Fig. 4). The pH values in all trials increased sharply within 10 min and then decreased gradually. The increase in pH might be explained by the production of hydroxyl ions at the cathode, and the decrease might be attributed to the consumption of hydroxyl anions as well as the production of HOCl [12]. The production and consumption of HOCl during the electrolysis also caused the variation in pH. The final pH in trial 19 was 6.8, which fell within the optimum pH range (pH 6.5–7.5) for methanogenesis [31], and was slightly higher than 6, the optimum pH for bioethanol production [32]. Hence, neutralization was hardly needed to bring about fermentation after the electrochemical treatment.

Moreover, a set of controlled experiments was carried out at initial pH values of 6, 7, 8, and 9. The profiles of the reducing sugar concentrations at different initial pH are shown in Fig. 6. As observed, the concentration of reducing sugars at pH 7 was lower than those of the other solutions (Fig. 6). At 180 min, the concentrations of reducing sugars at pH 6, 7, 8, and 9 were 0.261, 0.100, 0.300, and 0.290 mg mL⁻¹, respectively. Glucose and fructose have been reported to be the predominant water-

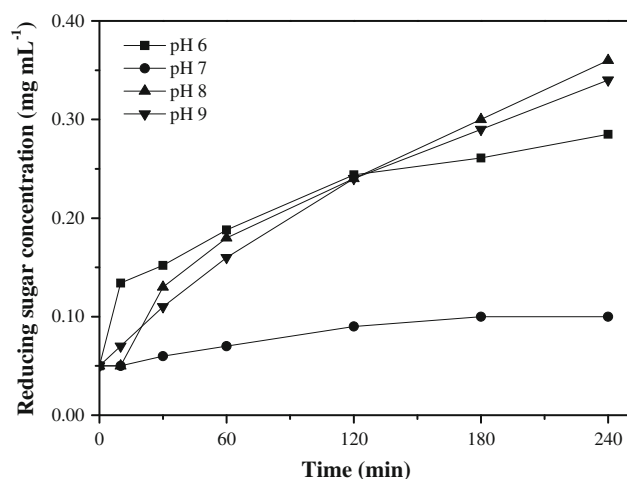


Fig. 6 Reducing sugar concentration at pH 6, 7, 8, and 9, at 20 °C

soluble components of corn stover, accounting for 30–46 % of the dry weight of extracts (4–12 % of the dry weight of feedstock) [33]. The dissolution of sugars was insignificant at pH 7 because of a lack of polar molecules and chemical reactions. The concentration of reducing sugars at pH 7 leveled off after 120 min (0.100 mg mL^{-1}), and was lower than the concentration at any other pH. There was no significant difference in reducing sugar concentrations at pH 6, 8, and 9, and the largest difference between pH 6 and 8 was only 0.049 mg mL^{-1} at 180 min. At a lower pH of 6, more hydronium ions were generated, which facilitated the degradation of hemicelluloses to the corresponding oligosaccharides. The ester bonds between the hemicelluloses and lignin are easily dissociated under moderate alkaline conditions [30]; therefore, the carbohydrates could be dissolved because of the dissociation of the highly ordered structure [2]. Thus, the variation in pH during electrolysis had a positive effect on the production of reducing sugars.

3.4 Morphological analysis

Figure 7 shows the SEM images of corn stover before and after electrolysis in trial 19. As evidenced from images, the raw biomass was compact, rigid, and highly ordered (Fig. 7a). However, the material structure became loose, polyporous, and disordered, and cellulose was exposed (Fig. 7b) after electrolysis, indicating that the lignocellulosic structure was destroyed and strongly modified during electrolysis. This change in the structure of lignocelluloses made the reducing sugars leached easily.

XRD analyses were conducted to investigate the CrI of cellulose [6]. In this study, the heights of the main peak (I_{002}) and the minimum value between the main and secondary peaks (I_{am}) were measured at 22° and 18.2° (2θ), respectively (Fig. 8). The CrI of the corn stover sample treated in trial 19 decreased from 0.4396 to 0.3493. Lignin, hemicelluloses, and cellulose were oxidized, leading to the exposure of cellulose, which was in agreement with Fig. 7b. The decrease in the CrI value indicated that the crystalline part of cellulose and amorphous part of lignocelluloses were oxidized, resulting in the disruption of the cellulose crystalline structure, which was one of the main purposes of the electrochemical conversion of lignocelluloses. Notably, the increase in CrI has been reported several times. Pang et al. [34] studied the pretreatment of corn stover using the stream explosion (SE) method for 5 min, and reported that the CrI increased from 0.290 to 0.576. Liu et al. [35] also reported the increase in CrI from 0.543 to 0.631 at 160°C by pretreatment with FeCl_3 for 20 min. Furthermore, the increase in CrI had no relevance with the overall carbohydrate degradation [21]. The SE pretreatment is thought to change the cellulose crystalline structure by disrupting inter/intramolecular hydrogen bonding among the cellulose chains, while the Fe^{3+} ion could react with lignocelluloses. Both the above methods were

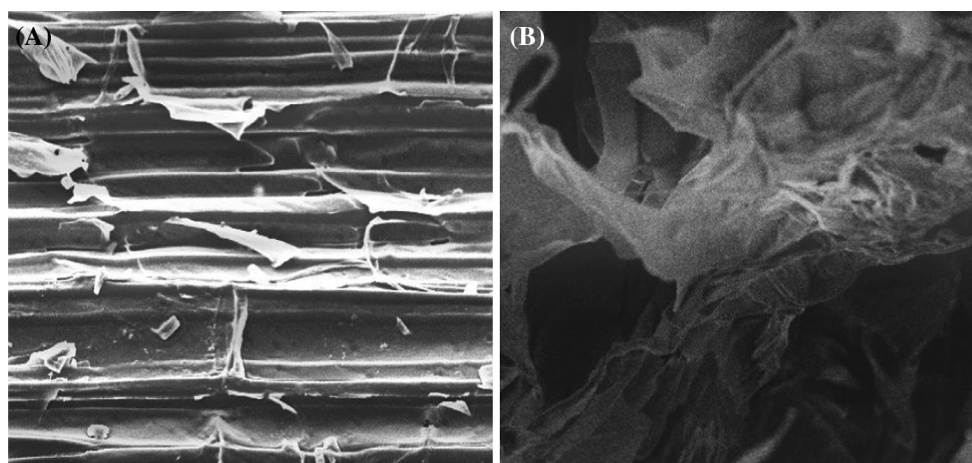


Fig. 7 SEM images of corn stover **a** before and **b** after electrochemical treatment at 500 magnification

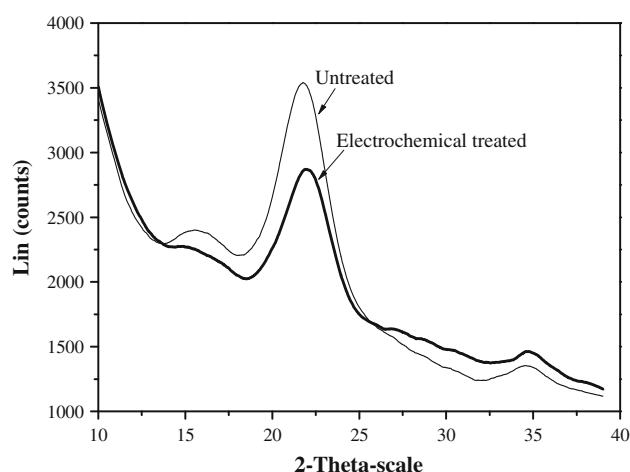


Fig. 8 XRD patterns of corn stover before and after the electrochemical treatment

efficient in removing lignin and hemicelluloses, thus enhancing the crystallinity of the obtained corn stove [34, 35].

4 Conclusions

The electrochemical conversion of corn stover was effective in the degradation of lignocellulosic material for further processing. The recovery of reducing sugars reached 0.610 mg mL^{-1} under the optimum operating conditions of ES, current density, and NaCl addition of 10 mm, 30 mA cm^{-2} , and 2000 mg L^{-1} , respectively, and a treatment time of 180 min, as obtained by the Taguchi methodology. The electrolysis reaction was dominated by indirect oxidation processes as a result of HOCl formation. The increasing temperature and variation in pH were beneficial to the production of the reducing sugars during electrolysis. Under the optimal conditions, the cellulose present in corn stover was successfully uncovered via destruction of the lignocellulosic structure, resulting in a decrease in the CrI from 0.4396 to 0.3493 after electrochemical treatment.

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